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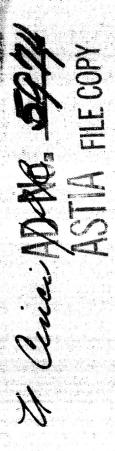
SCIENTIFIC AND TECHNICAL INFORMATION

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APPLIED SCIENCE RESEARCH LABORATORY
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NO

DEVELOPMENT OF NEW POLYMERS FOR AIRCRAFT APPLICATION

Navy Bu Aer Contract NOa(s) 52-090 c

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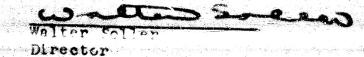


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Summary

- A. Chloroprene-Methacrylic Acid (C-MA) Copolymers
 - 1. Curing Studies

In view of the promising results obtained in the last Cornell tests (see Report No. 5), considerable time during this period has been devoted to the further study of organic curing agents. A series of diamines, imines and polyhydrox-phenols now have been evaluated, allowing the films to cure 14 days at room temperature. In general, the films possessed good tensile strength and elongations, but showed higher permanent set than those cured with metal oxides. (see Tables I, II, and III) The most effective of the organic curing agents tested thus far include benzidine, o-and p-phenylenediamines, diphenylguanidine (DFG), diamisidine and 2-amino-4-nitrophenol.

2. Cornell Tests

The tenth series of Cornell specimens comprising fourteen panels has been prepared and submitted for evaluation. (Table IV) The eleven C-MA topcoat panels were all air-cured with various diamines and/or DPG. Three of the panels employed a chloroprene-methacrylamide topcoat which has not been tested at Cornell previously. In the C-MA

series, the earlier lack of homogeneity and possible deleterious effects of the heat-cure have been eliminated. The tensile strength of the topcoats varies from 2900 to 5800 p.s.i.; therefore, a good indication of the effect of this property upon rain-erosion resistance should be obtained. Panel 10-A employing methacrylamide copolymer with an aircure using Goodyear accelerator 983-C will give a comparison with a like C-MA cure tested in the previous ninth Cornell series.

3. Effect of Water Immersion

In view of the fact that C-MA copolymer coatings previously have failed through bubbling on the Cornell rain erosion tester, water immersion tests of the films have been continued. (see Report No. 5) Costings approximately 5 mil thick were prepared on a standard C-MA primer. These coatings were kept at room temperature not less than a month before the immersion tests were conducted. (Table VI)

Upon immersion in water for 24 hours at 30°C, the films containing conventional rubber accelerators, and also catechol, para-toluidine and phenyi-B-naphthylamine, showed some water absorption as indicated by the color change of the coating. This change, however, was reversible as the films acquired their original color on standing in air. Secondly, the adhesion between the topcoat and the primer was weakened on immersion.

The films which had given the lowest compliances in

the creep study also were best in apparent resistance toward water absorption. Films containing para-phenylene diamine, DADPM, benzidine, and diphenyl-guanidine retained their original color and were excellent in intercoat adhesion. These tests indicate that coatings of low water sensitivity can be obtained using diamines as curing agents at room temperature.

4. The Creep Behaviour of C-MA Copolymers

In view of the previously reported failure to acquire correlation between creep behaviour and rain erosion data, (rain erosion series No. 9) lacquers tested for creep behaviour have been confined to the ones resulting in completely homogeneous films.

In connection with the study of promising air-curing agents, C-MA copolymer (AK-20) creep behaviour has been studied when cured with some 15 organic agents. (Figure 1) Also tensile properties, including elongation and ASTM permanent set have been determined. (Table VI)

The results from the creep tests seem to divide the organic agents into two groups. First, various diamines, diphenylguanidine, phloroglucinol and Goodyear Accelerator 958-C result in cured coatings after standing for 14 days. The cure probably results from salt formation between the carboxyl and the amino groups. The second class of substances, including most conventional accelerators, seem to act as plasticizers by increasing the compliance as compared with

pure gum stock.

Creep curve obtained with para-phenylenediamine cure has considerably lower compliance than the other diamines. This curve, however, will probably fall in line with the other diamines if equivalent molar quantities rather than equivalent weights are used.

A similarly effective cure has been realized with phloroglucinol. It is believed to be significant that the creep curve (compliance versus log time) is a straight line, (run No. 46) while diamines give a curve for the similar plot. Buchdahl and Nielsen have indicated that for some elastomers, a change in slope of the creep curve (log compliance versus log time) indicates a change in molecular mechanism of creep during the experiment. Accordingly, it may be that different mechanisms of cure are indicated here by the different types of curves obtained. Further investigation of this is in progress.

In comparing the creep and tensile properties of a given system, it appears that a low compliance is associated with a low ASTM set. Less consistently, the tensile increases and elongation decreases as compliance decreases. (Table VI)

The effect of heat on C-MA copolymer gumstock was determined. Creep behaviour of the gum stock was studied after 1, 2, 6 and 26 hours heating at 120 degrees C. (Figure II) The corresponding tensile properties also were determined. (Table VII) It was of interest to note that no improvement

Rolf Buchdahl and Lawrence E. Nielsen, Journal of Applied

in tensile strength was realized on heating, while the compliance decreased as expected on increasing the time of bake.

E. Chloroprene - Methacrylamide Copolymers

Additional curing studies have been conducted on the chloroprene-methac lamide copolymers with poly hydroxy aromatics. All provided reasonable but not outstanding high-temperature cures; the air cure results were not as high as with Goodyear Accelerator 983C.

In order to gain further insight into the nature of the copolymer, monomer relative reactivity ratios were determined both in solution and in emulsion. The results obtained were as follows: in solution at 50°C, n. = 5.5± 1.0, $n_{\rm m} = 0.05 \pm .05$; in emulsion at 30°C, $n_{\rm c} = 20 \pm .05$ 10, ~ = .03 ± .03. The greater difference in reactivity observed in emulsion presumably results from the large difference in water solubility. From the observed reactivity values in emulsion both integral and differential distribution curves have been plotted for a 40 weight percent methacry-. lamide charge. These indicate considerable heterogeneity of composition; for a 60% conversion polymer, roughly 1/3 would contain no more than 3 to 42 percent methacrylamide. 1/3 would contain $4\frac{1}{2}$ to 9 percent, $1/\epsilon$ would have a composition between 9 and 14 percent and the remainder would contain 14 to 29 percent.

Further investigations of the chloroprene-acrylonitrile copolymer have been conducted to study composition, curing and reinforcement. Good tensile strengths have been observed up to 24 percent acrylonitrile. The highest tensile strength without reinforcement was observed at 24 percent acrylonitrile; at the s composition, free films exhibited the following properties: tensile strength 3630 p.s.i.; elongation at break, 560 percent; permanent set 12 percent. Further improvement in tensile strength was observed with the addition of hard processing channel black. Twenty-five parts black raised the tensile strength to 4690 p.s.i. and decreased the elongation to 470 percent; the permanent set observed was 10 percent.

Various cures that proved successful for the methacrylamide copolymer were also tested for the acrylonitrile
copolymer. Tensile strengths above 3000 p.s.i. were obtained
for both an 8 part phloroglucinol cure and for the 6-2-2,
Zimate, magnesia, sulfur cure. No room temperature cures
were studied.

Program

Investigation of the sir-cure formulations similar to those in the present report will be continued. Results of the 10th Cornell series should give an indication of the relative merits of the various curing agents and, thus, assist in the further development of optimum coating properties. Creep studies of the C-MA copolymers will be continued with the objective of relating fundamental polymer properties to rain erosion resistance. Additional investi-

gation of the properties of chloroprene-methacrylamide copolymers also is planned.

Experimental

- A. Chloroprene-methacrylic Acid Copolymers
 - 1. Evaluation of Curing Agents

The effectiveness of various organic curing agents on C-MA, Gates Neoprene and Hypalon S-2 coatings are summarized in tables I, II, and III.

2. Cornell Test Panels

A new solvent system was employed in the preparation of the panels of the 10th Cornell series. (see Table IV) This 40-30-30 mixture by volume of methylisobutyl ketone, xylene and toluene seemed to dissolve the copolymer more quickly producing a nearly gel-free lacquer. Since the two monomers employed vary considerably in structure and physical properties, it seems reasonable that a ketone-aromatic hydrocarbon system is preferable to a mixed ketone system. This is further born out by the ready solubility of neoprene (100% chloroprene) in aromatic hydrocarbons.

3. Water Immersion Tests - Preparation of Specimens
Three-S aluminum panels (5 x 8 cm) were carefully
cleaned with cyclohexanone, and the standard C-MA primer
applied in about 1 mil thickness. The primer was subsequently cured for four hours at 120°C.

The topcoat lacquer (C-MA copolymer AK-20) to which the proper curing agents were added in solution, was

applied by pouring a small amount of lacquer on the primer.
The specimens were air dried on level steel plates.

B. Chloroprene-Methacrylamide Copolymers

Poth oven and room temperature cures were studied with a 10 percent methacrylamide copolymer at 61 percent conversion modified with 0.14 parts dodecyl mercaptan. The results are presented in Table VIII.

Table VIII
Curing Variations for the Chloroprene-Methacrylamide Copolymer

	Parts Bake	Tensile s	trength, p.s. 20 days
Agent 983c Catechol Pyrogallol Pyrogallol Phloroglucinol Phloroglucinol	0.9cc/gm 2 hrs @120°C	3210	3400
	8 2 hrs @120°C	3530	3660
	8 2 hrs &120°C	3780	4110
	8 air cure	2680	2900
	8 2 hrs @120°C	3890	3520
	8 air cure	2260	2280
Agent_	Elongation Break	<u>. 1</u>	ASTM Set
983c	900		15 3
Catechol	880		9 2
Pyrogallol	640		4 2
Pyrogallol	850		9
Phloroglucinol	530		5
Phloroglucinol	720		10

Neither air cure was comparable to that previously obtained with Goodyear Accelerator 983c. Several of the temperature cures approached the tensile strength obtained with the 6-2-2, zimate, magnesia, sulfur cure.

To study the bulk reactivity ratios for the chloroprenemethacrylamide system, polymerizations were conducted in methyl ethyl ketone at 50°C with 0.5 part benzoyl peroxide as initiator. After a polymerization time of 46 hours, the monomeric chloroprene was stripped off under vacuum. Residues were dissolved in methyl ethyl ketone and precipitated by pouring into an excess of water. This solution and precipitation was repeated to insure removal of the methacrylamide monomer. Polymers were dried to constant weight in vacuo at 45-50°C, and analyzed for chloride. The results are tabulated below.

Table IX

Solution Polymerization Data for the Chloroprene-Methacrylamide Copolymer

Wt. % Methacrylamide in charge	Conversion %	Wt. % Methacrylamide in Copolymer
19.4	9.3	5.7
39.0	10.0	12.5
59.0	8.5	16.5
69.1	6.8	24.5
79.4	4.8	35.9
89.6	5.0	61.8

From this data, reactivity ratios in solution were calculated using the method of intersections developed by Mayo and Lewis. Conversion was corrected for by the following equation which was also developed by these workers.

$$r_{2} = \frac{\log \frac{M_{2}^{\circ}}{N_{2}} - \frac{1}{P} \log \frac{1 - P \frac{M_{2}}{M_{2}}}{1 - P \frac{M_{2}^{\circ}}{M_{2}^{\circ}}}}{\log \frac{M_{1}^{\circ}}{M_{1}} + \log \frac{1 - P \frac{M_{2}^{\circ}}{M_{2}^{\circ}}}{1 - P \frac{M_{2}^{\circ}}{M_{2}^{\circ}}}}$$

^{2.} F.R. Mayo and F.M. Lewis, J Am Chem Soc 56, 1594 (1944)

where $p=(l-r_i)/(l-r_2)$, M, and M₂ are the moles of monomers unpolymerized at the end of the reaction and M₂ and M₂ are the moles of monomers charged.

The ratios as determined in solution were 5.5 * 0.5 for chloroprene and 0.05 * 0.05 for methacrylamide. These same values should also hold in bulk polymerization.

For emulsion system, a series of low conversion polymers was also prepared for reactivity calculation, but analyses proved inconsistent, probably as a result of errors introduced by the short-stop and other ingredients of the emulsion recipe. Calculations were then based on the following data obtained mostly at higher conversions.

Table X

Composition-Conversion Data in Emulsion for Reactivity Calculations

Wt. % Methacrylamide in charge	Conversion, %	wt. % Methacrylamide in polymer
15	68	2.5
25	68 . 68	2.6 3.7
3 0 4 0	34	4.9 7.9
40	61 51	10.5
50 70	31	17.4

This data is in conformity with the reactivity of 20 ± 10 for chloroprene and .03 ± .03 for methacrylamide. It should be noted that in this work reactivity ratios in emulsion have been interpretted following the treatment of Wall.

^{3.} Wall, F.T., J Am Chem Soc. 72, 476, 4769 (1950)

They differ from the corresponding ratios in bulk by the distribution coefficients of the monomers between the phases present and are consequently a function of the monomer-water ratio. The reactivities determined here were for a 1:2 monomer to water ratio.

taneous and average polymer composition are plotted as a function of conversion; the average composition curve was calculated using the followin equation of mayo and Lewis:

$$\frac{M_{2}}{M_{1}^{\circ}} = \left(\frac{M_{1}}{M_{1}^{\circ}}\right)^{2} \qquad = \frac{n_{2}}{m_{1}} + \frac{M_{2}^{\circ}/m_{1}^{\circ}}{m_{2}^{\circ}} + 1$$

The instantaneous composition curve was obtained as the slope of a plot of moles of methacrylamide in the polymer as a function of the moles of polymer. Instantaneous composition curves have been utilized by Skeist⁴ as an indication of copolymer heterogeneity; the difference in compositions at 25 and 75 percent conversions provides a numerical measure of the dispersion of composition of the copolymer. It will be seen that the spread from 5 to 99 percent methacrylamide is indicative of considerable composition dispersion.

^{4.} Skeist, I., J Am Chem See 66, 1781 (1945)

strikingly in the differential distribution curve, Figure 4; this was constructed from the slope of the instantaneous composition curve plotted against this composition. The area under this differential distribution curve between any two instantaneous compositions represents the fraction of the monomer charge that has been converted to polymer of that composition range. From this curve, it is apparent that for a 60 percent conversion polymer, roughly 1/3 of the polymer has a composition between 3 and 4½ percent methacrylamide, another 1/3 between 4½ and 9 percent, 1/6 between 5 and 14 percent and the remaining 1/6 between 14 and 29 percent.

C. Chloroprene-Acrylonitrile Copolymers

A series of chloroprene-acrylonitrile copoliners has been prepared without wereaptan modification to furnish further information on the effect of composition on physical properties. The results are tabulated below using a cure of 5 parts zinc oxide, 4 parts magnesia, and 2 parts Ethyl Selenac and a bake of 3 nours at 140°C.

Effect of Composition on Conversion for Chloroprene-Acrylonitrile Copolymers

Wt. % Acrylonitrile in copolymer	Tensile Strength	Elong. at Break, %	ASTM Set
14.7	3290	750	3 .
17.2	3300	630	42
18.6	327	660	6
19.3	3350	670	- 8
	ÜşÜ	600	10
24.2	პ€30 ─	560	12
20.4	3040	380	17

Although highest tensile strengths were observed in the vicinity of 24 percent acrylonitrile, permanent set was much improved at lower acrylonitrile contents.

Additional curing experiments were conducted to see if the mixed oxide - Ethyl Selenac cure can be improved upon.

Results are summarized in Table MII.

Miscellaneous Curing Studies with the Chloroprene Acrylonitrile Copolymer

Agent	<u>Bake</u>	Tensile Strength psi	Elong. at Break, %	ASTM Set
5 ZnO 4 MgO 2 Et. Selenac	3 hr @140	3200	600	10
6 Lt. Zimate 2 MgO 2 S	2 hr ©120	2830	•	
6 Et. Zimate 2 MgO 2 S	3 hr @140	3300	720	13
Goodyear 983c .9 cc/gm 8 Phloroglucinol 8 Pyrogailol	2 hr @120 2 hr @120 2 hr @120	1910 3510 2440	9 15 - 850	21 11
4 MgO 8 Et. Selenac	2 hr @120	2610	670	11

Physical properties appeared to be effected by the conditioning period after bake. On the basis of the following data, the tensile strength of the phloroglucipol cure decreases with time whereas it improves for both the 6-2-2- cure and for the mixed oxide-Ethyl Selenac Cure.

Table XIII

Effect of Conditioning Time on Tensile Strength

A	gent		Bake	4	Tensile days	Strength, 11 days	psi 18 days
4		3 Selenac	hrs @140°C	29	920	3120	3200
2	Et. Z MgO S	imate 2	hrs @120°C		2180	2760	2830
8	Phlor	oglucinol	2 hrs @120°C.		3510	3260	2840

The highest tensile strengths for the chloropreneacrylonitrile copolymers were obtained with carbon black
reinforced films. Hard processing channel black was milled
into an 18.6 percent acrylonitrile copolymer in amounts up
to 25 parts. The results are tabulated below:

Table XIV

Effect of Carbon Black Loading on Physical Properties for Chloroprene-Acrylonitrile Copolymers

Chloroprene-Acrylonitrile Copolymers										
Parts	HPC	Black	Tensile	Strength	psi	Elong.	at	Break %	ASTM	Se t
	0		3	130		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	650)	5불	
	2		36	500			700)	7통	
	5		3'	740			700)	73	
	10		39	920			610)	8	
	20		4	650			580		10	
	25		40	690			470		10	

High carbon black loading is detrimental to both elongation at break and permanent set.

Table I

Air-Cure of C-MA Lacquers by Organic Curing agents

	Amount	Tensile	Strength at	Break, po-
uring Agent			4370	
	6 pts.		4640	
enzidine	10 pts.		4500	
3 - Dec 3	pts. plus	3 pts.	Appendix surveyed to the first to the	
	6 pts.		3300	
PG plus 1 pt paraffin	6 pts.	u	2770	
-Aminophenol	6 pts.		2400	
hloroglucinoi	6 pts.		2350	
aminopyridine			3200	
examethylene tetramine	6 pts.		3500	
ntenisidine	6 pts.		2900	
a-nhenvlene diamine	6 pts.		5780	
- shenvlene dlamino	e nte		2250	
2-aminobenzothiazoro	6 pts.		2030	
o aminogran13016	6 pts.		3980	
2-amino-4-nitrophenol	6 pts.		3200	
DADPM	S pts.		1790	
Toluidine	g bre.		4400	
DPG	€ pts.			

Table II

Air-Cure of Gates Coating by Organic Curing gents

	Amount	Tensile	Strength at	Break,	psi
Curing Agent	en e		1700		
Dianisidine	6 pts.		2000		
DPG	6 pts.		2050		
DADPM . o-phenylene diamine	6 pts.	To See The Property Con-	3030 3200		
p-phenylene diamine	6 pts.	# C			ra jeji jagarit

Table III

Air-Cure of Hypalon S-2 by Organic Curing Agents

4	Emount	Tensile Streng	th at Break, psi
Curing Agent		lus 3 pts.	1730
DPG plus MBT			
DPG plus MBT plus DAD	PM 3 pts.p	lus 3 pts.plus	3 pts. 2810

Notes

-16-

- . 10% methacrylamide at 62% conversion
- Chloroprene-methacrylic acid copolymer of 55.04% conversion and an acid content
- 3. Gates Enginearing Company's commercial polymer lacquer N-79
- 4. Dupont's chlorosulfonated polythene nolymer dissoved in methylethyl ketone and toluene.

Table V

Immersion of C-WA Costings

Specimen		ond. of coating efore immersion*	Cond. of coating after immersion for 24 hrs at 30°C water**
7	Thionex	1	i
<u>, , , , , , , , , , , , , , , , , , , </u>	Goodyear Acc.983-	1555	and the state of t
<u> </u>	Methyl tuads		
<u> </u>			and the second second of the second s
9	Ethyl Selenac	Salaman (1977) A salaman kana da kana d Manana da kana	r various set setter have a see a The see a
	DADPM		
I	Catechol	<u> </u>	2
J	o-aminophenol	₫	2-3
K	dianisidine	<u> </u>	en en la completa. La cométa del callaba de l'Agua (ella casa del Agrada) a basa de casa de callaba de la come
L	Diphenylguanidine	3	2-3
M-	Phloroglucinol	2	2
N	Phenyl-B-naphthyl		
	amine		1-2
ń.	p-phenylene-diami	ne 3	3.
D .	benzidine	3	3
· · · · · · · · · · · · · · · · · · ·	B -nitroso naphth	ol 2-3	
Ř	p-toluidine		

#1. Film tacky - fingerprints remain on coating; good primer topcoat adhesion.

2. Film somewhat tacky, and does not retain gloss on rubbing.

3. Films free of tack and reasonably glossy.

**1. Films turned to different shades of green; adhesion failure between topcoat and primer can be initiated by rubbing with finger.

2. Some discoloration of the coating; hard to initiate

adhesion failure.

3. No apparent discoloration; good inter-coat adhesion.

***Methyl tuads crystallized out in the film as viewed with a 50 X microscope.

Table VI

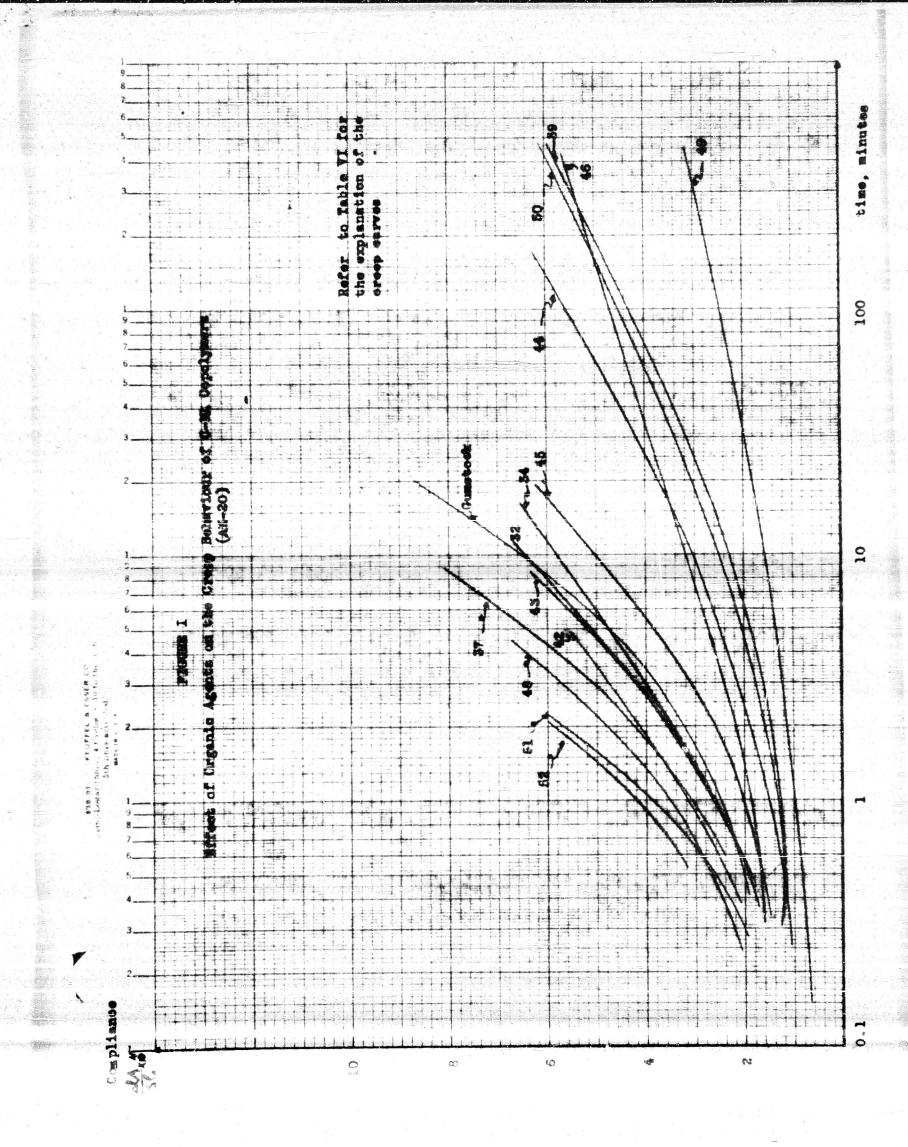
Effect of Organic Agents on C-MA copelymer (AK-20)

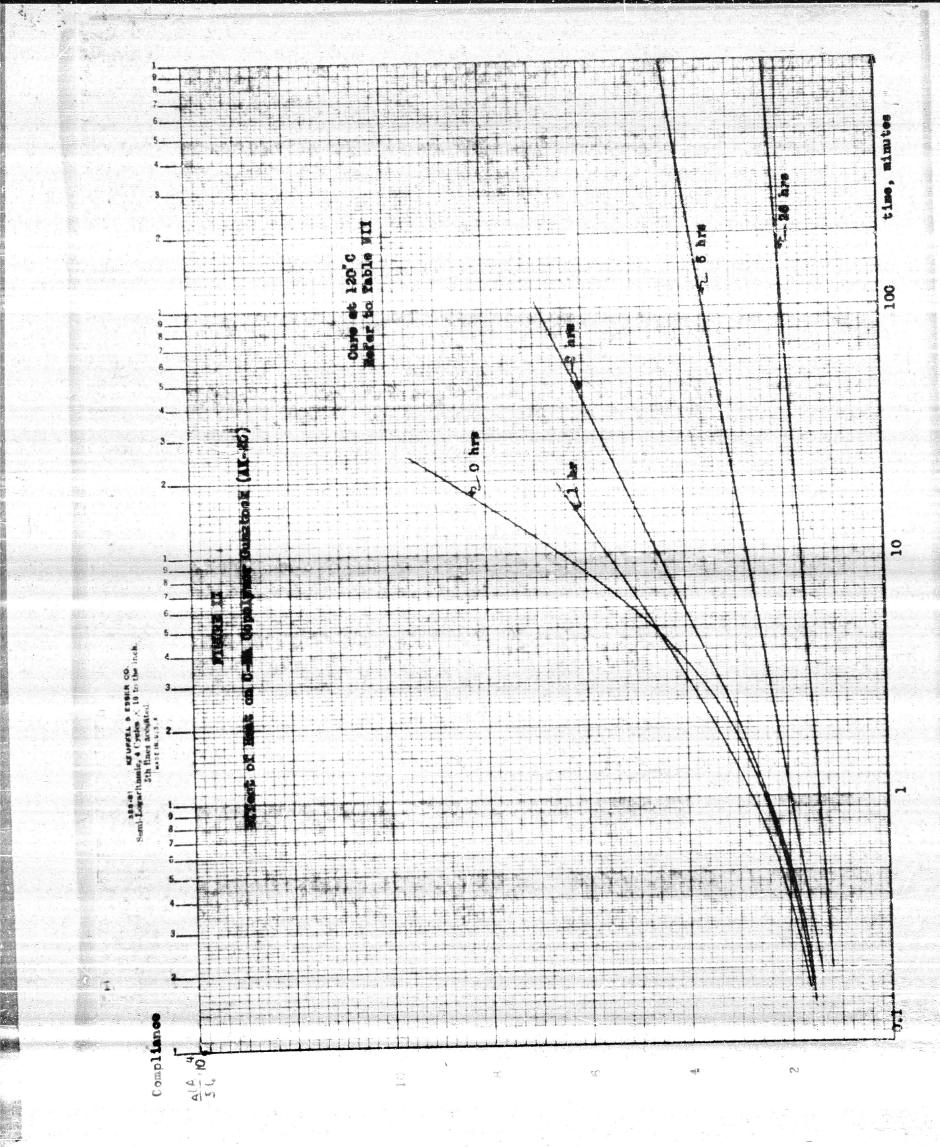
Spe ci men	Run No.	Organic Agent 5 parts	Tensile psi	Elong.	A.S.T.M. Set,%	l min. Recovery,%
	29	Acc 808 - 16 parts	1490	1580	57	13
A. D	30	Captax	1370	1550	83	10
	31	Altax	1350	1650	78	7.
C	32	Thionex	1570	1500	65	6
E	. 34	Acc 938-C-Goodyear	1590	1250	51	6
	36	Methyl tuads	1310	1300	66	- 6
F G	37	Ethyl Selenac	1450	1420	72	5
	39	DADPM	2620	1170	36	5
H	42	Catechol	1630	1300	69	6
ά	43	o-amino phenol.	1720	1300	68	5
K	44	dianisidine	2660	1260	44	4
	45	DPG (diphenyl-				
ط	'FO	guanidine)	2240	1160	64	4'
ermonen er i de	46	Phloroglucinol	2700	1240	45	3
IF N	48	Phenyl-8-naphthylamine		1400	65	5
^	49	p-phenylene-diamine	5430	990	26	5
0 P	50	Benzidine base	3770	1020	35	4
	51	6-nitroso naphthol	1500	1240	70	5
Q R	52	p-toluidine	2280	1300	64	5

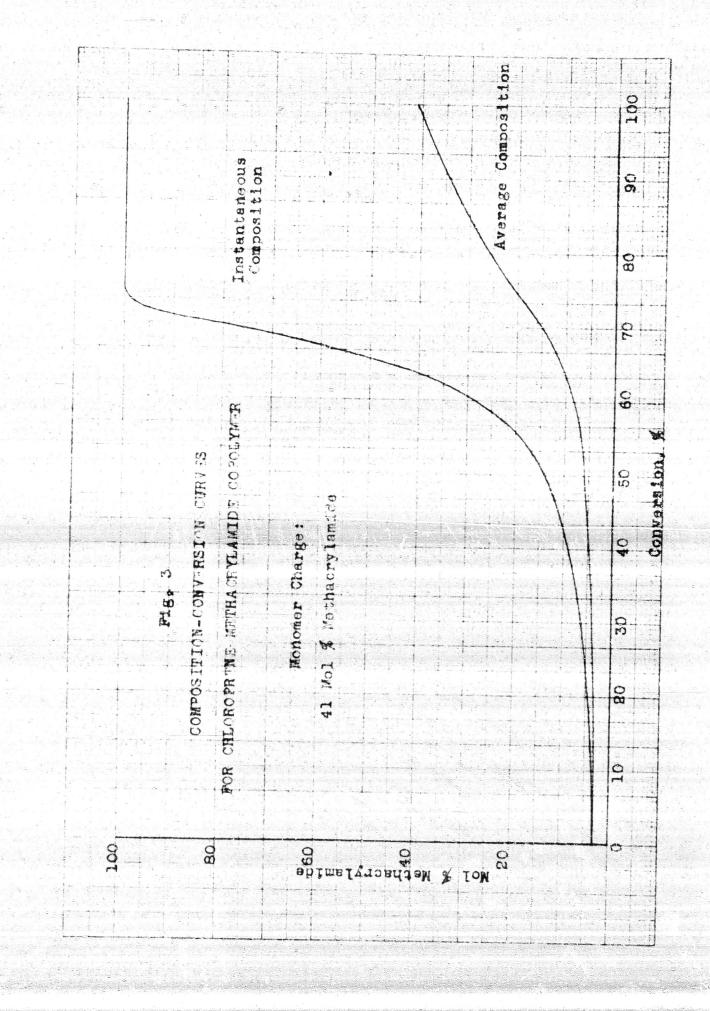
Table VII

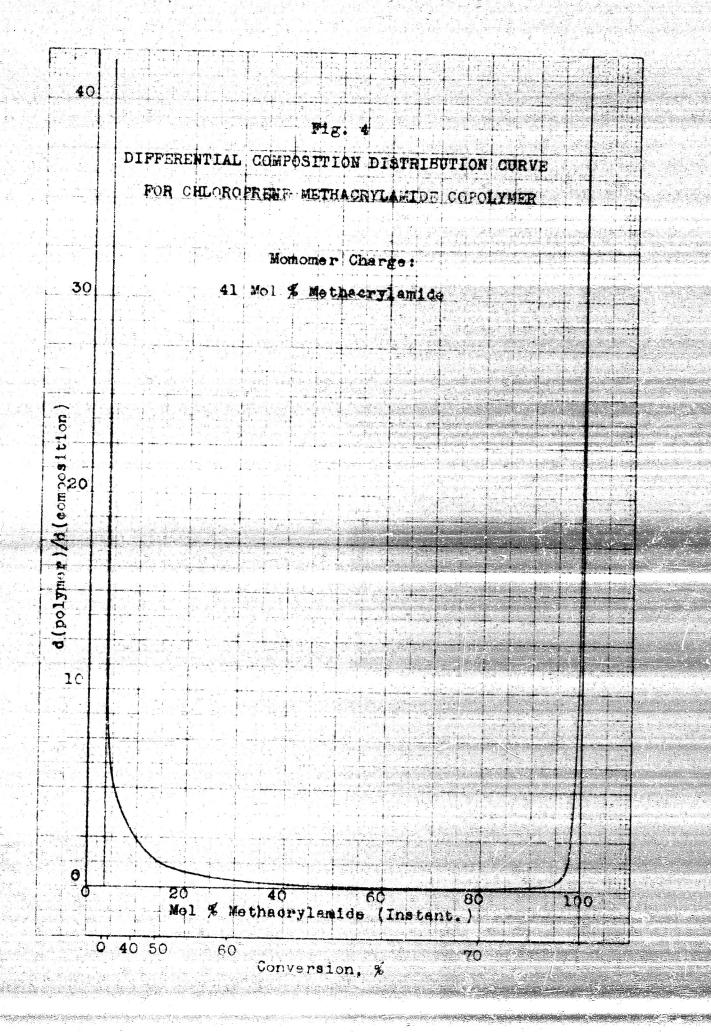
Effect of Heat on C-MA Copolymer Gumstock (AK-20)

Run No.	Cure	Tensile psi	Elong.	A.S.T.M. Set, %	l min. Recovery, %
38	14 days, air cure	1565	1420	74	6
40	1 hr. 120°.0	1700	1360	45	
41	1 hr. 120° C 2 hrs. 120° C	1680	1210	35	
33	6 hrs. 120° C	1670	1060	15	
35	26 hrs. 120° C	1350	890	8	









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